

Chinese Patent No. 1352204 A

BEST AVAILABLE COPY

---

Job No.: 6194-94965

Translated from Chinese by the Ralph McElroy Translation Company  
910 West Avenue, Austin, Texas 78701 USA

PEOPLE'S REPUBLIC OF CHINA  
NATIONAL OFFICE OF INTELLECTUAL PROPERTY  
INVENTION AND PATENT PUBLICATION JOURNAL  
PATENT NO. 1352204A

Int. Cl.<sup>7</sup>: C08F 10/00  
C08F 4/80

Filing No.: 01140471.X

Filing Date: December 10, 2001

Publication Date: June 5, 2002 (026)

No. of pages of claims: 4

No. of pages of explanation: 11

No. of pages of accompanying figures: 0

PREPARATION METHOD OF POLYMERIZED CATALYSTS WITH DUAL ACTIVITY  
CENTERS FOR POLYMERIZATION OF OLEFINS

Inventors: Guo-xin JIN and  
Chang-kun LIU

Applicant: Chinese Academy of Science  
Applied Chemistry Research  
Institute

Address: c/o Gui-Zhen CAO  
159 Ren-min Da Dào  
Chang-chun City, Jilin Province  
130022

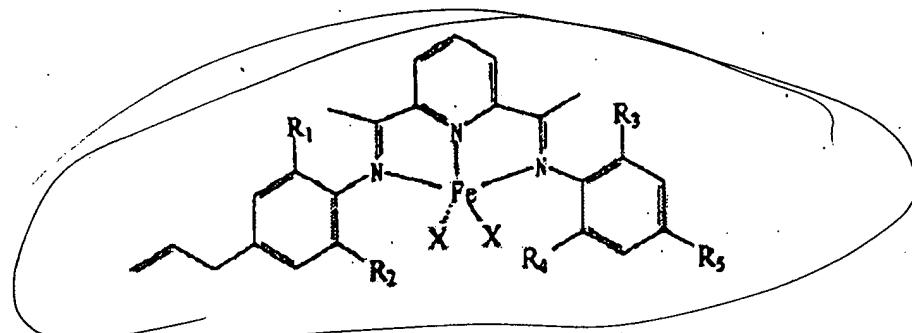
Abstract

This invention pertains to a preparation method of polymerized catalysts with dual activity centers for polymerization of olefins, and said method carries out reaction of iron-pyridine diimide compounds containing alkenyl groups and metallocene compounds containing alkenyl groups with styrene by the action of an initiator to link the metal compounds

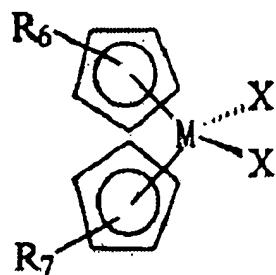
to polymer chains via C-C $\alpha$  bonding to give polymerized catalysts with dual activity centers for polymerization of olefins, which are represented by formula [P(Com Fe-co-S-co-Com M)], where P represents copolymers, S represents polystyrene, co represents copolymerization, Com Fe represents iron catalysts, and Com M represents metallocene catalysts. The dual activity centers demonstrate catalytic activity simultaneously during the polymerization process and exercise a synergistic effect, and this type of catalyst for catalyzing ethylene polymerization possesses high activity and produces polymers with characteristic properties and is suitable for gas-phase and slurry polymerization processes.

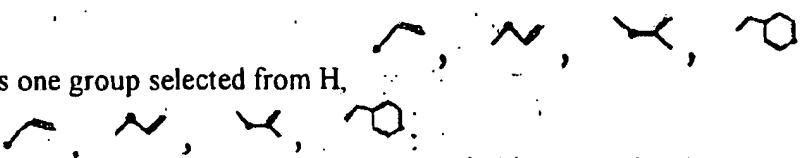
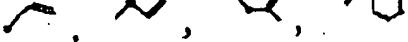
Claims

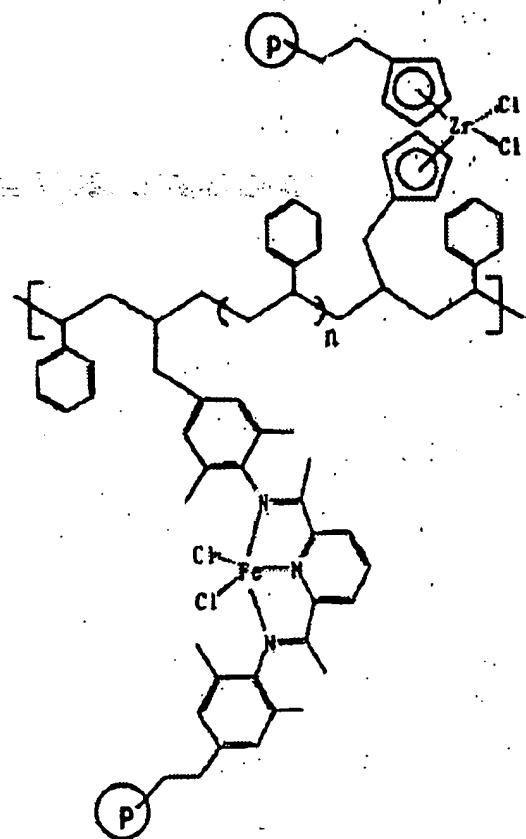
1. A polymerized catalyst with dual activity centers for olefin polymerization, comprising components A and B, characterized in that component A is represented by formula [P(Com Fe-co-S-co-Com M)], where P represents copolymers, S represents polystyrene, co represents copolymerization, Com Fe represents iron catalysts, and Com M represents metallocene catalysts, and the specific structural formula is as follows:



Com Fe: R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are one group selected from H, CH<sub>3</sub>, i-Pr and t-Bu, respectively; R<sub>5</sub> is H or allyl, and X is Cl or Br;



Com M:  $R_6$  is one group selected from H, ;  $R_7$  is one group selected from ; M is Ti, Zr or Hf; X is Cl or Br;



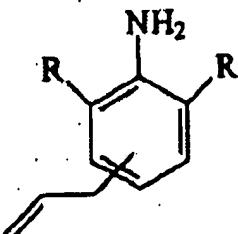
A model of the polymerized catalysts with dual activity centers for olefin polymerization is:  $R_1 = R_2 = R_3 = R_4 = CH_3$ ;  $R_5 = R_6 = R_7 = allyl$ ; M = Zr; X = Cl.

Component B is methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or pentafluorophenylborane.

2. A preparation method of polymerized catalysts with dual activity centers for olefin polymerization, characterized in that the preparation procedure for the catalysts is as follows:

1). Preparation of alkenylarylamines

The structural formula is:



R is one group selected from H, Me, i-Pr and t-Bu

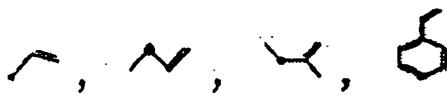
Arylamine and alkenyl chloride or alkenyl bromide at molar ratio of 2:1 are heated and reacted to give N-alkenylarylamine, yield 30.0-84.3%, and the N-alkenylarylamine together with excessive amount of  $ZnCl_2$  are heated and refluxed in toluene solvent to cause rearrangements and give 4-alkenylarylamine or 2-alkenylarylamine. Yield 25.2-70.9%.

## 2). Preparation of alkenyl-cyclopentadiene

The structural formula is:



R is one group selected from



Equimolar amounts of cyclopentadiene and alkenyl chloride or alkenyl bromide are reacted in aqueous NaOH solution in the presence of tetrabutylammonium bromide as a phase transfer agent to give cyclopentadiene with an alkenyl group as a substituent. Yield 40-70%.

## 3). Preparation of alkenyl iron catalysts Com Fe

First, a 2-step, acid-catalyzed condensation reaction of 2,6-diacetylpyridine and alkenyl amine is carried out to give a corresponding pyridine diimide ligand; if said ligand has symmetrical structure, the 2-step condensation can be accomplished in one step, where the molar ratio of the amine and 2,6-diacetylpyridine is 2:1. A pyridine diimide compound having an alkenyl group can then be prepared from the reaction of the obtained pyridine diimide ligand with  $FeX_2$ . Yield 90-95%.

The reaction procedure of the preparation is as follows:

Alkenylarylamine and 2,6-diacetylpyridine condense to form a tridentate pyridine diimide ligand in methanol solvent using formic acid as the catalyst. Preparation of Com Fe is carried out under the protective condition of an oxygen-free and anhydrous environment using high-purity argon; pyridine diimide ligand and  $FeCl_2 \cdot 4H_2O$  are mixed at 1.05:1 molar ratio for 2-3 h at room temperature using 30-40 mL tetrahydrofuran solvent to give a blue solution, which

is vacuum concentrated, and a blue precipitate is obtained by adding n-hexane, which is filtered and vacuum dried, yield 90-95%.

#### 4). Preparation of alkenyl metallocene catalysts Com M

First, a corresponding lithium salt of alkenyl cyclopentadiene is prepared from equal moles of alkenyl cyclopentadiene and n-butyllithium, and to prepare an alkenyl metallocene catalyst with symmetric structure, alkenyl cyclopentadiene lithium salt and  $MCl_4$  at molar ratio of 2:1 are reacted; to prepare an alkenyl metallocene catalyst with an asymmetric structure, equal moles of two alkenyl cyclopentadiene lithium salts and equal moles of  $MCl_4$  are reacted. Yield 60-75%.

The reaction procedure of the preparation is as follows:

Alkenyl cyclopentadiene is added to tetrahydrofuran solvent, and an equimolar amount of n-butyllithium is added dropwise while keeping in an ice-salt bath, followed by agitating for 2-3 h at room temperature. A tetrahydrofuran solution of an equal mole of  $MCl_4$  is then added slowly, where the solution turns deep red, which is agitated for 6-8 h at room temperature, followed by distilling off the solvent and adding toluene and centrifuging to remove lithium salt, from which solvent is eliminated by suction, and washing several times with n-hexane gives the product, yield 60-75%.

#### 5). Preparation of polymerized catalysts with dual activity centers for olefin polymerization

Under anhydrous and oxygen-free conditions, iron catalyst having alkenyl group Com Fe, metallocene catalyst having alkenyl group Com M, styrene, azobis diisobutyrenitrile are added in sequence to dried toluene and mixed until homogeneous, followed by carrying out polymerization on a water bath and using n-hexane as a precipitating agent, to give a polymer product as a solid powder, which is washed 3 times with n-hexane and dried to give a polymerized catalyst with dual activity centers for olefin polymerization.

3. Application of the polymerized catalysts with dual activity centers for olefin polymerization, characterized in that the catalyzed polymerization of ethylene is carried out under anhydrous and oxygen-free conditions, in that the reaction system comprises 100-2000 mL toluene, to which methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), and the polymerized catalyst with dual activity centers at molar ratio to MAO or MMAO of  $Al/(Fe+M) = 350-3500$ , and ethylene 1-20 atm are added in sequence, and the reaction is carried out for 1 h at -15-80°C; an ethanol solution containing 1wt% hydrochloric acid is used to quench the reaction, from which the obtained product is filtered and washed several times with ethanol, followed by vacuum drying for 24 h at 40°C.

## Explanation

Preparation method of polymerized catalysts with dual activity centers for olefin polymerization

## Technical field

This patent pertains to catalysts for olefin polymerization, particularly pertains to polymerized catalysts with dual activity centers for olefin polymerization.

The present invention also pertains to a preparation method of the aforementioned catalysts;

The present invention still pertains to the application of the aforementioned catalysts for olefin polymerization, particularly for ethylene polymerization.

## Background of the technology

Production of polyolefins is the core of modern polymer material industry, and catalysts are the nuclei of polyolefin production. In recent years, development of catalysts for olefin polymerization has reached a point far beyond the range of the traditional catalysts having pre-transition metals of the IVB group as the activity center, and catalysts of post-transition metals for olefin polymerization have become the focus of research (Lettl S.D, Johnson L.K, Brookhart M, Chem. Rev., 2000, 100, 1169; Britovsek G.J.P, Gibson V.C, Wass D.F, Angew. Chem. Int. Ed, 1999, 38, 428). However, the traditional pre-transition metal catalysts are still demonstrating a very significant effect on modern industrial production, and how to combine the advantages of pre-transition metal catalysts and post-transition metal catalysts to prepare polyolefin materials with new structural and property characteristics has become an important research direction. Chinese Patent Applications (98125651.1, 1998; 00121820.4, 2000) disclose a preparation method of polymerized metallocene catalyst for olefin polymerization and a preparation method of polymerized post-transition metal "post-MAO" catalyst for olefin polymerization, respectively. The two methods are both suitable for supporting catalysts with a single activity center on polymers.

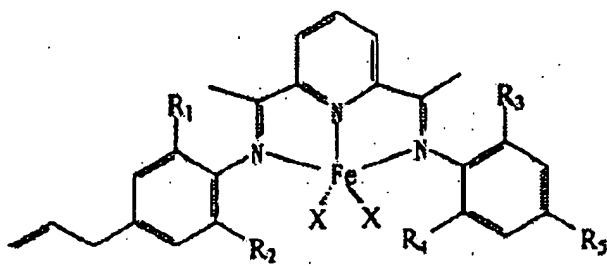
## Content of the invention

The objective of the present invention lies in providing a polymerized catalyst with dual activity centers for olefin polymerization, and said catalysts have two activity centers in the structures, and the two activity centers exercise catalytic effects simultaneously when catalyzing olefin polymerization, demonstrating a synergistic effect.

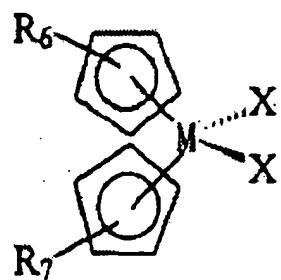
Another objective of the present invention lies in providing a preparation method of polymerized catalysts with dual activity centers for olefin polymerization, and said method has a simple procedure and processing is easy to control.

Still another objective of the present invention lies in providing polymerized catalysts with dual activity centers for olefin polymerization, particularly for ethylene polymerization, where the obtained polyolefin products have characteristic properties.

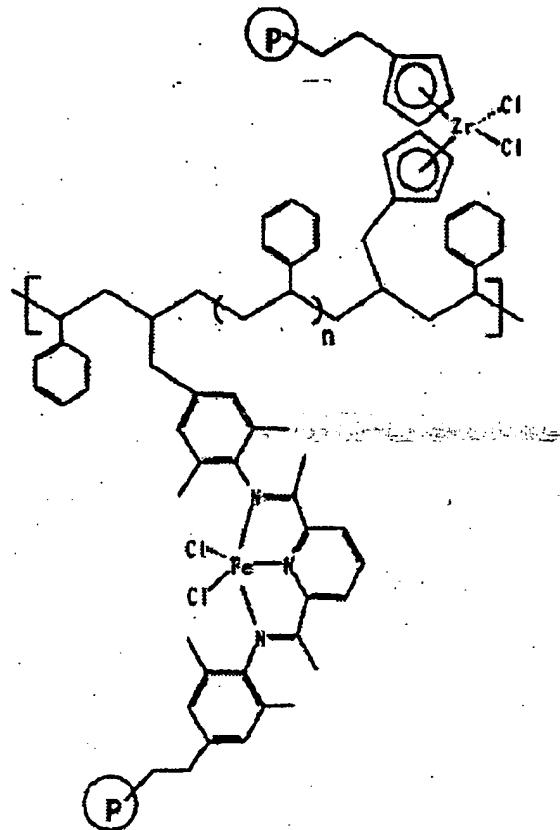
The catalysts with dual activity centers for olefin polymerization prepared by the present invention comprise A and B components to achieve the aforementioned objectives, characterized in that component A is represented by formula [P(Com Fe-co-S-co-Com M)], where P represents copolymers, S represents polystyrene, co represents copolymerization, Com Fe represents iron catalysts, and Com M represents metallocene catalysts, and the specific structural formula is as follows:



Com Fe: R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are one group selected from H, CH<sub>3</sub>, i-Pr and t-Bu, respectively; R<sub>5</sub> is H or allyl, and X is Cl or Br;



Com M: R<sub>6</sub> is one group selected from H, , , , ; R<sub>7</sub> is one group selected from , , , ; M is Ti, Zr or Hf; X is Cl or Br;



A model of the polymerized catalysts with dual activity centers for olefin polymerization is:  $R_1 = R_2 = R_3 = R_4 = CH_3$ ;  $R_5 = R_6 = R_7 = allyl$ ;  $M = Zr$ ;  $X = Cl$ .

Component B is methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or pentafluorophenylborane.

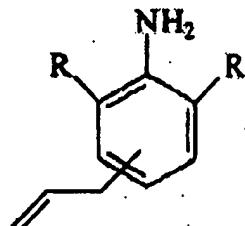
The polymerized catalysts with dual activity centers provided by the present invention for olefin polymerization have not been reported in literature or patents.

The preparation method of polymerized catalysts with dual activity centers for polymerization of olefins provided by the present invention carries out reaction of iron-pyridine diimide compounds containing alkenyl groups and metallocene compounds containing alkenyl groups with styrene by the action of an initiator to link the metal compounds to polymer chains via C-Ca bonding to give polymerized catalysts with dual activity centers for polymerization of olefins.

The preparation procedure of the catalysts is as follows:

#### 1. Preparation of alkenylarylamines

The structural formula is:

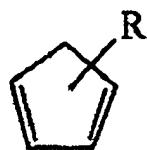


R is one group selected from H, Me<sub>3</sub>, i-Pr and t-Bu

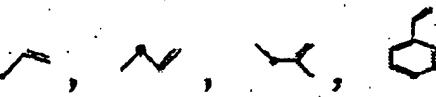
Arylamine and alkenyl chloride or alkenyl bromide at molar ratio of 2:1 are heated and reacted to give N-alkenylarylamine, yield 30.8-84.3%, and the N-alkenylarylamine together with an excessive amount of ZnCl<sub>2</sub> are heated and refluxed in toluene solvent to cause rearrangements and give 4-alkenylarylamine or 2-alkenylarylamine. Yield 25.2-70.9%.

## 2. Preparation of alkenyl cyclopentadiene

The structural formula is:



R is one group selected from



Equimolar amounts of cyclopentadiene and alkenyl chloride or alkenyl bromide are reacted in aqueous NaOH solution in the presence of tetrabutylammonium bromide as a phase transfer agent to give cyclopentadiene with an alkenyl group as a substituent. Yield 40-70%;

## 3. Preparation of alkenyl iron catalysts Com Fe

First, a 2-step, acid-catalyzed condensation reaction of 2,6-diacetylpyridine and alkenyl amine is carried out to give a corresponding pyridine diimide ligand; if said ligand has a symmetrical structure, the 2-step condensation can be accomplished in one step, where the molar ratio of the amine and 2,6-diacetylpyridine is 2:1. A pyridine diimide compound having an alkenyl group can then be prepared from the reaction of the obtained pyridine diimide ligand with FeX<sub>2</sub>. Yield 90-95%.

The reaction procedure of the preparation is as follows:

Alkenylarylamine and 2,6-diacetylpyridine condense to form tridentate pyridine diimide ligand in methanol solvent using formic acid as catalyst. Preparation of Com Fe is carried out under the protective condition of oxygen-free and anhydrous environment using high purity argon; Pyridine diimide ligand and FeCl<sub>2</sub>•4H<sub>2</sub>O are mixed at 1.05:1 molar ratio for 2-3 h at room temperature using 30-40 mL tetrahydrofuran solvent to give a blue solution, which is vacuum concentrated, and a blue precipitate is obtained by adding n-hexane, which is filtered and vacuum dried, yield 90-95%.

## 4. Preparation of alkenyl metallocene catalysts Com M

First, a corresponding lithium salt of alkenyl-cyclopentadiene is prepared from equal moles of alkenyl cyclopentadiene and n-butyllithium, and to prepare an alkenyl metallocene catalyst with symmetric structure, alkenyl cyclopentadiene lithium salt and  $MCl_4$  at molar ratio of 2:1 are reacted; to prepare an alkenyl metallocene catalyst with an asymmetric structure, equimolar amounts of two alkenyl cyclopentadiene lithium salts and equal mole of  $MCl_4$  are reacted. Yield 60-75%.

The reaction procedure of the preparation is as follows:

Alkenyl cyclopentadiene is added to tetrahydrofuran solvent, and an equimolar amounts of n-butyllithium is added dropwise while keeping in an ice-salt bath, followed by agitating for 2-3 h at room temperature. A tetrahydrofuran solution of an equimolar amounts of  $MCl_4$  is then added slowly, where the solution turns deep red, which is agitated for 6-8 h at room temperature, followed by distilling off the solvent and adding toluene and centrifuging to remove lithium salt, from which solvent is eliminated by suction, and washing several times with n-hexane gives the product, yield 60-75%.

#### 5. Preparation of polymerized catalysts with dual activity centers for olefin polymerization

Under anhydrous and oxygen-free conditions, iron catalyst having alkenyl group Com Fe, metallocene catalyst having alkenyl group Com M, styrene, azobisisobutyrenitrile are added in sequence to dried toluene and mixed until homogeneous, followed by carrying out polymerization on a water bath and using n-hexane as a precipitating agent, to give a polymer product as a solid powder, which is washed 3 times with n-hexane and dried to give polymerized catalysts with dual activity centers for olefin polymerization.

The polymerization of olefins, particularly the polymerization of ethylene catalyzed by the polymerized catalysts with dual activity centers provided by the present invention for olefin polymerization is conducted under anhydrous and oxygen-free conditions, in that the reaction system comprises 100-2000 mL toluene, to which methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), and the polymerized catalyst with dual activity centers at molar ratio to MAO or MMAO of  $Al/(Fe+M) = 350-3500$ , and ethylene 1-20 atm are added in sequence, and the reaction is carried out for 1 h at -15-80°C; an ethanol solution containing 1wt% hydrochloric acid is used to quench the reaction, from which the obtained product is filtered and washed several times with ethanol, followed by vacuum drying for 24 h at 40°C.

The specific application examples are as follows:

##### Application Example 1: Preparation of alkenyl arylamines

A mixture of 2,6-diisopropylaniline 0.2mol and allyl chloride 0.1 mol is heated and refluxed for 10 h, followed by cooling and standing for 12 h, which is then added to 400 mL

water and alkalified with sodium hydroxide solution until alkaline, and the reaction mixture is extracted with diethyl ether. Vacuum distillation gives N-allylaniline, 18.33 g, yield 84.3%. N-allyl aniline 0.084 mol and an excessive amount of  $ZnCl_2$  are added to 100 mL toluene solvent, which is refluxed for 5 h in an argon atmosphere, and the mixture is poured into an aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned organic phase of diethyl ether extraction, followed by drying over anhydrous magnesium sulfate, and vacuum distillation gives 4-allylaniline, 12.92 g, yield 70.9%.

#### Application Example 2: Preparation of alkenylaryl amines

A mixture of aniline 0.24 mol and allyl bromide 0.12 mol is heated and refluxed for 8 h, followed by cooling and standing for 10 h, which is then added to 200 mL water and alkalified with a sodium hydroxide solution, and the reaction mixture is extracted with diethyl ether. Vacuum distillation gives N-allylaniline, 8.645 g, yield 54.1%. N-allylaniline 0.065 mol and an excessive amount of  $ZnCl_2$  are added to 200 mL toluene solvent, which is refluxed for 8 h in an argon atmosphere, and the mixture is poured into an aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned organic phase of diethyl ether extraction, followed by drying over anhydrous magnesium sulfate, and vacuum distillation gives 2-allylaniline, 2.18 g, yield 25.2%.

#### Application Example 3: Preparation of alkenyl amines

A mixture of 4-tert-butylaniline 0.2 mol and allyl chloride 0.1 mol is heated and refluxed for 9 h, followed by cooling and allowing to stand for 11 h, which is then added to 300 mL water and alkalified with sodium hydroxide solution, and the reaction mixture is extracted with diethyl ether. Vacuum distillation gives N-allyl-2-tert-butylaniline, 5.67 g, yield 30.0%. N-allyl-2-tert-butylaniline, 0.03 mol, and an excessive amount of  $ZnCl_2$  are added to 50 mL toluene solvent, which is refluxed for 6 h in an argon atmosphere, and the mixture is poured into an aqueous sodium hydroxide solution after cooling. The organic layer is separated and the insoluble material in the lower layer is dissolved in hot concentrated hydrochloric acid, which is decanted into the aforementioned organic phase of diethyl ether extraction, followed by drying over anhydrous magnesium sulfate, and vacuum distillation gives 4-allyl-2-tert-butylaniline, 3.54 g, yield 62.4%.

Application Example 4: Preparation of alkenyl cyclopentadiene

100 mL 33% NaOH, 0.5 mol cyclopentadiene and 0.5 mol allyl chloride are added in sequence to a glass Schlenk bottle, and the mixture is stirred for 2 h on an ice bath in the presence of 2 g tetrabutylammonium bromide as a phase transfer agent, followed by stirring for 6 h at room temperature. The oil phase is washed until neutral, followed by drying over anhydrous potassium carbonate, and vacuum distillation gives allyl cyclopentadiene, 36.75 g, yield 70.0%.

Application Example 5: Preparation of alkenyl cyclopentadiene

110 mL 33% NaOH, 0.6 mol cyclopentadiene and 0.5 mol 3-bromo-1-butene are added in sequence to a glass Schlenk bottle, and the mixture is stirred for 2 h on an ice bath in the presence of 3 g tetrabutylammonium bromide as a phase transfer agent, followed by stirring for 7 h at room temperature. The oil phase is washed until neutral, followed by drying over anhydrous potassium carbonate, and vacuum distillation gives 3-cyclopentadienyl-1-butene, 26.78 g, yield 45.01%.

Application Example 6: Preparation of alkenyl cyclopentadiene

110 mL 33% NaOH, 0.5 mol cyclopentadiene and 0.5 mol 4-bromostyrene are added in sequence to a glass Schlenk bottle, and the mixture is stirred for 2 h on an ice bath in the presence of 2.5 g tetrabutylammonium bromide as a phase transfer agent, followed by stirring for 6.5 h at room temperature. The oil phase is washed until neutral, followed by drying over anhydrous potassium carbonate, and vacuum distillation gives styryl cyclopentadiene, 33.40 g, yield 40.0%.

Application Example 7: Preparation of alkenyl iron catalysts Com Fe

Tridentate pyridine diimide ligand compound  $C_{39}H_{51}N_3$  is prepared from 4-allylaniline and 2,6-diacetylpypyridine by a condensation reaction in methanol solvent using formic acid as a catalyst. Preparation of Com Fe is carried out under the protective conditions of oxygen-free and anhydrous environment using high-purity argon. Said pyridine diimide ligand compound, 4.0 mmol, and  $FeCl_2 \cdot 4H_2O$  3.8 mmol are agitated for 2 h in 30 mL tetrahydrofuran solvent at room temperature to give a blue solution, which is vacuum concentrated, and a blue precipitate is obtained by adding n-hexane, which is filtered and vacuum dried, to give  $C_{39}H_{51}N_3FeCl_2$ , 2.48 g, yield 95%.

Application Example 8: Preparation of alkenyl iron catalysts Com Fe

Tridentate pyridine diimide ligand compound  $C_{30}H_{35}N_3$  is prepared from 2-tert-butyl-4-allylaniline, 2,6-dimethylaniline and 2,6-diacetylpyridine by condensation reaction in methanol solvent using formic acid as catalyst. Preparation of Com Fe is carried out under the protective conditions of oxygen-free and anhydrous environment using high purity argon. Said pyridine diimide ligand compound, 1.51 mmol, and  $FeCl_2 \cdot 4H_2O$  1.44 mmol are agitated in 40 mL tetrahydrofuran solvent for 4 h at room temperature to give a blue solution, which is vacuum concentrated, and a blue precipitate is obtained by adding n-hexane, which is filtered and vacuum dried, to give  $C_{30}H_{35}N_3FeCl_2$  0.731 g, yield 90%.

Application Example 9: Preparation of alkenyl iron catalysts Com Fe

Tridentate pyridine diimide ligand compound  $C_{27}H_{27}N_3$  is prepared from 2-allylaniline, 2,6-dimethylaniline and 2,6-diacetylpyridine by a condensation reaction in methanol solvent using formic acid as a catalyst. Preparation of Com Fe is carried out under the protective conditions of oxygen-free and anhydrous environment using high-purity argon. Said pyridine diimide ligand compound 2.27 mmol and  $FeCl_2 \cdot 4H_2O$ , 2.16 mmol, are agitated in 35 mL tetrahydrofuran solvent for 2.5 h at room temperature to give a blue solution, which is vacuum concentrated, and a blue precipitate is obtained by adding n-hexane, which is filtered and vacuum dried, to give  $C_{27}H_{27}N_3FeCl_2$ , 1.044 g, yield 93%.

Application Example 10: Preparation of alkenyl metallocene catalysts Com M

Allyl cyclopentadiene 4.14 mmol is added to tetrahydrofuran solvent and an equimolar amount of n-butyllithium is added dropwise on an ice water bath, followed by agitating for 2 h at room temperature, and a mole equivalent solution of  $ZrCl_4$  in tetrahydrofuran is added slowly, where the solution turns deep red, which is agitated for 6 h at room temperature, followed by distilling off the solvent and adding toluene and centrifuging to remove lithium salt, from which solvent is eliminated by suction, and washing several times with hexane gives the product,  $C_{16}H_{16}ZrCl_2$ , 0.574 g, yield 75%.

Application Example 11: Preparation of alkenyl metallocene catalysts Com M

3-Cyclopentadienyl-1-butene 2.17 mmol and allyl cyclopentadiene 2.17 mmol are added to tetrahydrofuran solvent and 4.34 mol of n-butyllithium are added dropwise on an ice-water bath, followed by agitating for 3 h at room temperature, and a mole equivalent solution of  $TiCl_4$  in tetrahydrofuran is added slowly, where the solution turns deep red, which is agitated for 8 h at room temperature, followed by distilling off the solvent and adding toluene and centrifuging to

remove lithium salt, from which solvent is eliminated by suction, and washing several times with hexane gives the product,  $C_{18}H_{18}TiCl_2$ , 0.444 g, yield 60%.

Application Example 12: Preparation of alkenyl metallocene catalysts Com M

Styryl cyclopentadiene 1.79 mmol and cyclopentadiene 1.79 mmol are added to tetrahydrofuran solvent and 3.58 mol of n-butyllithium are added dropwise on an ice-water bath, followed by agitating for 2.5 h at room temperature, and a mole equivalent solution of  $ZrCl_4$  in tetrahydrofuran is added slowly, where the solution turns deep red, which is agitated for 7.5 h at room temperature, followed by distilling off the solvent and adding toluene and centrifuging to remove lithium salt, from which solvent is eliminated by suction, and washing several times with hexane gives the product,  $C_{18}H_{14}ZrCl_2$ , 0.431 g, yield 61.4%.

Application Example 13: Preparation of polymerized alkenyl catalysts with dual activity centers for olefin polymerization

Under anhydrous and oxygen-free conditions, 0.2 mmol iron catalyst  $C_{39}H_{51}N_3FeCl_2$  obtained in Application Example 7 and 0.7 mmol metallocene catalyst  $C_{18}H_{16}ZrCl_2$  obtained in Application Example 10, styrene 5 mL and azobisisobutyrenitrile 1.0 wt% are added in sequence to dried toluene and mixed until homogeneous, and copolymerization is carried out for 10 h at 80°C on a water bath, followed by cooling to room temperature and centrifuging, and n-hexane is added to the supernatant as a precipitant to give a solid powder, which is washed 3 times with n-hexane and dried. The iron content is determined to be 0.256 wt%, and the zirconium content is 1.57 wt%.

Application Example 14: Preparation of polymerized alkenyl catalysts with dual activity centers for olefin polymerization

Under anhydrous and oxygen-free conditions, 0.5 mmol iron catalyst  $C_{30}H_{35}N_3FeCl_2$  obtained in Application Example 8 and 0.5 mmol metallocene catalyst  $C_{18}H_{14}ZrCl_2$  obtained in Application Example 12, styrene, 8 mL, and azobisisobutyrenitrile 1.0 wt% are added in sequence to dried toluene and mixed until homogeneous, and copolymerization is carried out for 11 h at 80°C on a water bath, followed by cooling to room temperature and centrifuging, and n-hexane is added to the supernatant as a precipitant to give a solid powder, which is washed 3 times with n-hexane and dried. The iron content is determined to be 0.214 wt%, and the zirconium content is 0.419 wt%.

**Application Example 15: Preparation of polymerized alkenyl catalysts with dual activity centers for olefin polymerization**

Under anhydrous and oxygen-free conditions, 0.7 mmol iron catalyst  $C_{27}H_{27}N_3FeCl_2$  obtained in Application Example 9 and 0.4 mmol metallocene catalyst  $C_{17}H_{18}TiCl_2$  obtained in Application Example 11, styrene, 10 mL, and azobisisobutyrenitrile 1.0 wt% are added in sequence to dried toluene and mixed until homogeneous, and copolymerization is carried out for 1.2 h at 80°C on a water bath, followed by cooling to room temperature and centrifuging, and n-hexane is added to the supernatant as a precipitant to give a solid powder, which is washed 3 times with n-hexane and dried. The iron content is determined to be 0.532 wt%, and the zirconium content is 0.467 wt%.

**Application Example 16: Polymerization of ethylene**

Polymerization of ethylene is carried out under anhydrous and oxygen-free conditions. The reaction system comprises toluene 100 mL, to which methylaluminoxane, polymerized catalyst with dual activity centers obtained in Application Example 13 (0.02 g),  $Al/(Fe+Zr) = 350$ , and ethylene, 1 atm, are added in sequence, and reaction is carried out for 1 h at -15°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered and washed several times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 1.76 g polyethylene.

**Application Example 17: Polymerization of ethylene**

Polymerization of ethylene is carried out under anhydrous and oxygen-free condition. The reaction system comprises toluene 500 mL, to which modified methylaluminoxane, polymerized catalyst with dual activity centers obtained in Application Example 13 (0.02 g),  $Al/(Fe+Zr) = 1400$ , and ethylene, 5 atm are added in sequence and reaction is carried out for 1 h at 30°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered and washed several times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 19.25 g polyethylene.

**Application Example 18: Polymerization of ethylene**

Polymerization of ethylene is carried out under anhydrous and oxygen-free conditions. The reaction system comprises 2000 mL toluene, to which modified methylaluminoxane, polymerized catalyst with dual activity centers obtained in Application Example 14 (0.04 g),  $Al/(Fe+Zr) = 3500$ , and ethylene 4 atm are added in sequence, and reaction is carried out for 1 h at 45°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid,

and the obtained product is filtered and washed several times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 6.48 g polyethylene.

Application Example 19: Polymerization of ethylene

Polymerization of ethylene is carried out under anhydrous and oxygen-free conditions. The reaction system comprises 2000 mL toluene, to which methylaluminoxane, polymerized catalyst with dual activity centers obtained in Application Example 15 (0.02 g), Al/(Fe+Zr) = 1700, and ethylene, 20 atm, are added in sequence and reaction is carried out for 1 h at 80°C. The reaction is quenched using an ethanol solution containing 1% hydrochloric acid, and the obtained product is filtered and washed several times with ethanol, followed by vacuum drying for 24 h at 40°C, to give 21.74 g polyethylene.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**